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Abstract

The characterization and use of a palladium and iridium catalyst combination on several cathode substrates (carbon paper, porous nickel, titanium dioxide, carbon fibers) for metal-hydrogen peroxide semi-fuel cells are described. The Pd/Ir combination outperforms palladium alone or iridium alone on all of the substrates as determined by catalyst deposit stability, polarization curve Tafel slope and onset potential. Scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS) along with transmission electron microscopy (TEM) were used to establish the composition and structure of palladium and iridium clusters on the cathode substrate surfaces. Cyclic voltammetry was employed as the method of choice for deposition; however, constant potential deposition was also investigated. Several deposition parameters were investigated including deposition range, scan rate, and number of cycles. This paper will describe the optimum deposition conditions and the best catalyzed substrate as tested in a metal-hydrogen peroxide semi-fuel cell.

Keywords: Electrochemical cells, hydrogen peroxide, semi-fuel cells, catalysis, palladium and iridium.

Introduction

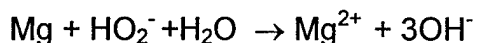
Aluminum anodes used in aqueous batteries with, for example, silver (II) oxide or air cathodes have been investigated extensively [1]. The use of a hydrogen peroxide catholyte in combination with an aluminum anode has been the subject of several studies carried out by the electric propulsion group at NUWC [2,3]. When aluminum is combined with hydrogen peroxide in a caustic electrolyte, the overall cell reaction is:



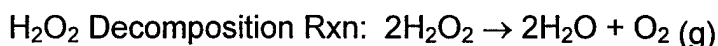
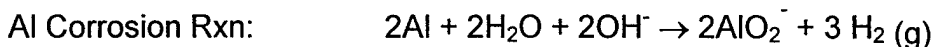
Operating cell voltages in the 1.2 - 1.7V range, depending on current density, have been routinely obtained. The Al - H₂O₂ electrochemical couple compares

favorably with the Al - AgO couple and other high energy density primary battery systems. An energy density of 360 Wh dm⁻³ is projected to be achievable for the Al - H₂O₂ solution phase catholyte system whereas an energy density of 290 Wh dm⁻³ is projected for a similarly configured Al - AgO system [2].

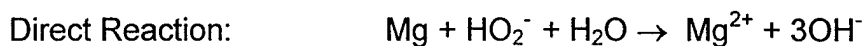
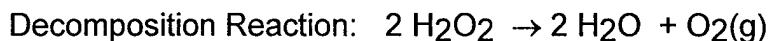
A parallel effort is also under investigation that is similar to the previous work by virtue of the commonality of the solution phase catholyte (H₂O₂), while different than the previous work by virtue of the magnesium anode in place of the aluminum anode[4,5]. In addition, this system will exclude the use of the sodium hydroxide in the seawater electrolyte; as well as focus on current densities below 50mA cm⁻². Preliminary calculations indicate that the elimination of the sodium hydroxide electrolyte and activation of the anode in pure seawater will enable an increase in specific energy of 50%, thus 250 Wh/lb, or 6-7 times that of silver-zinc. The overall cell reaction for the Mg-SFC is:



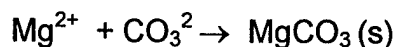
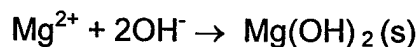
An ion diffusion membrane is not used in the semi-fuel cells studied to reduce complexity, weight and cost while increasing reliability and cell voltage. This approach, however, results in the catholyte being in direct contact with both the anode and the electrocatalytic cathode substrate. A direct, non-electrochemical, reaction will thus occur. Unless the rate of this direct reaction is low compared to the electrochemical anodic and cathodic reactions, the direct reaction will significantly reduce the overall efficiency of the cell. Additional reductions in efficiency can occur for an aluminum anode based cell due to a corrosion reaction of anode with hydroxide ions and the decomposition reaction of H₂O₂.



Unfortunately the theoretical open circuit potentials for the Mg-SFC system are reduced and the electrochemical performance is inhibited by the following parasitic reactions:



Precipitation Reactions:



Improved catalysis for the reduction of H_2O_2 should result in reductions of the direct and the decomposition reactions thus improving significantly the electrochemical efficiency of the cell.

Several catalysts have been investigated for use in fuel cells [6]. Many of these catalysts (including palladium and iridium independently) have been incorporated in carbon based pastes [7]. J.P. Collman and K. Kim have reported that iridium porphyrin complexes are very active catalysts [8]. Cox and Jaworski have used a palladium-iridium combination on a glassy carbon microelectrode for the quantitative determination of H_2O_2 [9]. A combination of palladium and iridium has been shown in the NUWC electric propulsion laboratories to improve the electrochemical efficiency for the reduction of H_2O_2 and to improve cell voltage relative to the use of a metallic silver cathode [10].

The studies described in this paper were directed at verification of the improved electrocatalytic behavior of a palladium-iridium combination, at stabilizing the Pd/Ir deposit on an appropriate substrate, at investigating a ternary system by incorporating bismuth (Bi) with the palladium and iridium deposit, at studying the best method of deposition, and optimizing the deposition parameters.

Experimental

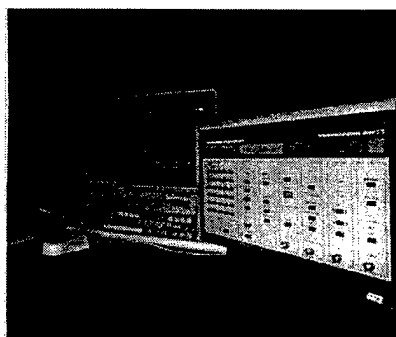
All chemicals used in this investigation were of reagent grade quality and were used as obtained from the supplier (Aldrich Chemicals or Fisher Scientific) without further purification. All solutions were prepared using glass distilled water. Reticulated nickel (Eltech Inc.; 100 pores per inch, 60 mils thick), carbon paper (E-Tek Inc., thickness 0.25mm), carbon cloth (E-Tek Inc., thickness 0.35mm), and reticulated vitreous carbon (RVC) (Electrosynthesis Inc, 10 pores

per inch, thickness 0.50mm) were all tested as electrode substrates. Several substrate pretreatment methods were evaluated and will be discussed in this paper.

The addition of titanium dioxide (TiO_2) as a slurry onto a Retic Ni substrate was made by weighing out 3.0 g of TiO_2 . The TiO_2 was then transferred into a mortar and pestle, 20 mL of methoxyethanol was added to the mortar along with 1 drop of Triton X. The TiO_2 was then ground until it dissolved. The electrode sample to be coated was either dipped into the TiO_2 or a nebulizer was used to spray the TiO_2 onto the electrode. In both cases the electrodes were placed into an oven where the temperature was ramped to 450°C in 30 minutes and held at 450°C for one hour.

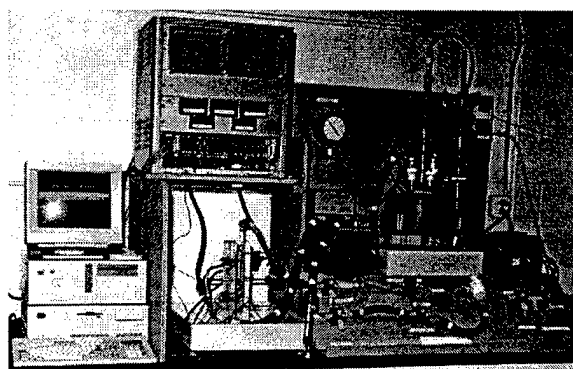
The simultaneous deposition of the palladium and iridium on the substrate was carried out by cyclic voltammetry at several deposition ranges. Deposition rates evaluated ranged from 1mV/s to 40 mV/s, and the number of cycles evaluated ranged from 5 cycles to 45 cycles. An EG&G Model 273A Potentiostat/Galvanostat (Figure 1) with a data acquisition system was utilized. The solution used for the deposition procedure was heated to 70°C and contained PdCl_2 , and Na_2IrCl_6 , (0.5mM to 4mM each) in a supporting electrolyte of 0.2M KCl, and 0.1M HCl. The concentration ratios of the PdCl_2 and Na_2IrCl_6 were also investigated and ranged from 4:1 to 1:4 Pd:Ir. A three-electrode cell consisting of the substrate working electrode, a Ag/AgCl reference electrode, and a spectroscopic grade carbon rod counter electrode was employed. The Model 273A Potentiostat and data acquisition system was used to record all polarization curves.

Figure 1. Potentiostat / Galvanostat Test Apparatus



Full cell performance was carried out using a 38 x 200 mm (1.5" x 8") cell made of plexi glass (Figure 2). A Vexar spacer maintained the cell gap at 0.7mm in the cell. The anode and cathode were mounted on individual current collector bus bars. The two electrodes were mounted vertically and were separated by the Vexar screen spacer. The catholyte and the electrolyte were pumped into the bottom of the cell, flowed between the anode and the cathode surfaces and exited at the top of the cell. The cell was incorporated into a closed loop flowing electrolyte apparatus consisting, in series, of a heated electrolyte reservoir, a peristaltic pump, a heat exchanging coil in a constant temperature bath to maintain temperature, the flow through cell and a return to the reservoir. Cell current was regulated by means of a multistep load resistance substitution box and a dynaload. Cell current, voltage, inlet and outlet temperatures, and evolved gas flow rate were simultaneously monitored and recorded by the computer data logging system. The software used for the data acquisition was Lab Tech Notebook.

Figure 2. Flow Through Cell Test Apparatus



The aluminum anode was an Alupower alloy designated EB50V. The electrolyte contained 3.0M NaOH, 0.5M H₂O₂ and 40g/L of sea salt. Its temperature was maintained at 55°C and the flow rate was 100cm³/min. For the magnesium-seawater electrochemical system, a magnesium anode (AZ61) was employed. The electrolyte consisted of 40 g/L sea salt, 0.5M H₂O₂ and 0.1M acid, at a temperature of 55°C.

Evolved gas was collected with a gas tight syringe from a "T" connection and rubber septum at the exit of the condenser tube located above the electrolyte tank. Gas samples were taken several times during a particular run. The gas samples were analyzed for H₂(g) and O₂(g) with a Hewlett Packard Capillary Gas Chromatograph Model 5890 Series II Plus equipped with an HP PLOT Molecular Sieve 5A column (30m x 0.32mm x 0.25µm film thickness) and a thermal conductivity detector.

The scanning electron microscopy was carried out using a JEOL USA Model 6300 instrument. The SEM working distance was 15 mm giving a resolution of 5.0nm. A Princeton Gamma Tech Energy Dispersive Spectrometer (EDS) was used for surface characterization. The detector was a Digital Sealed Light Element Si(Li) Spectrometer with a beryllium window. A Sun Sparc workstation with Integrated Microanalyzer for Imaging and X-Ray (IMIX) software was employed. Transmission electron microscopy data was obtained at the MIT Center for Material Science and Engineering with a VG Model HB603 Scanning Transmission Electron Microscope (STEM) and associated data acquisition hardware and software.

Results and Discussion

Selection of Appropriate Substrate:

Previous work has shown that the electrocatalyst when deposited on nickel foil yields poor stability and poor reproducibility [11]. Variations in performance were noticed from run to run. A high density carbon (HDC) obtained from Goodfellow,

Inc. had improved stability, reproducibility and performance over the nickel foil [9]. This material is commercially available in high purity but it is expensive.

Pd/Ir deposited on carbon cloth (E-Tek) had poor adhesion in all cases. As seen in Figure 3, the deposit is highly cracked and very flaky. The SEM micrographs for nickel foil and high density carbon are included in Figure 3 for comparison. The poor adhesion and coverage of the Pd/Ir is very evident on both nickel foil and carbon cloth.

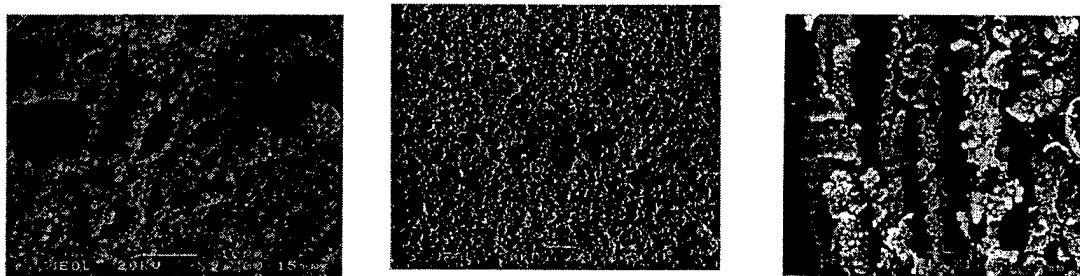


Figure 3. SEM micrographs of Ni Foil, High Density Carbon and Carbon Cloth catalyzed with Pd/Ir (800X, 1000X and 1000X respectively)

A carbon paper substrate (Spectracarb Porous Carbon Paper, E-Tek) was found to support the most uniform and adherent electrocatalytic surface is available commercially at a reasonable price, it is also the substrate for many of the electrodes available from E-Tek. This material has a high conductivity (0.005Wcm electrical resistivity), it is available in a range of thicknesses (0.002" to 0.150") and it is also available in range of sizes up to 60" X 60". A comparison of the catalytic performance of iridium alone, palladium alone and a palladium/iridium combination for the reduction of H_2O_2 in a sodium hydroxide, sea salt electrolyte at 55°C is presented in Figure 4. The superior performance of the combination of Pd/Ir over the entire current density range is clearly evident.

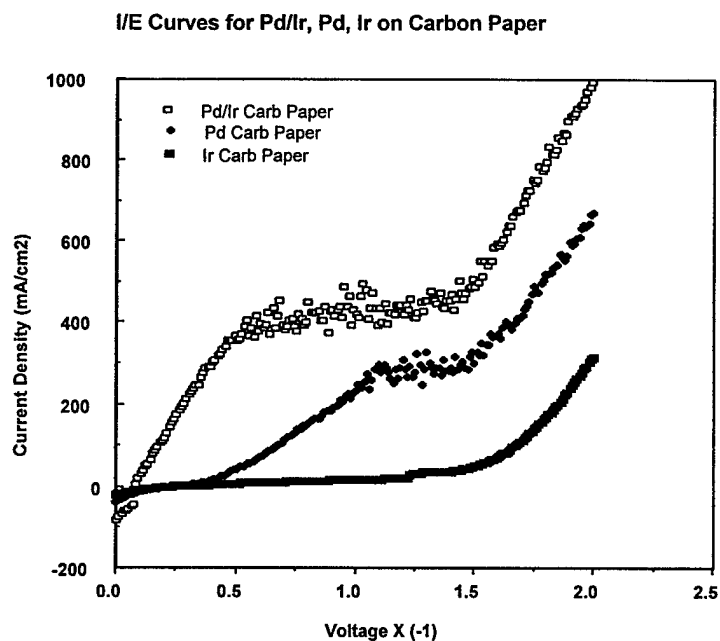


Figure 4. Current vs Potential Polarization Curve for Pd alone, Ir alone and Pd/Ir combination on Carbon Paper

Deposition Ranges

The several cyclic voltammetry deposition ranges that were evaluated to assess the adhesion and coverage of the Pd/Ir (1:2 ratio) deposit on carbon paper are listed in Table I.

Table I. Cyclic Voltammetry Deposition Ranges Evaluated

-0.15 to -0.30V	0.60 to 0.00V	1.20 to -0.30V
0.00 to -0.30V	0.60 to -1.3V	1.50 to -0.30V
0.00 to -0.50V	0.60 to -1.50V	1.50 to -0.50V
0.25 to -0.50V	1.00 to -0.50V	1.6 to -0.30V
0.40 to -0.3V	1.00 to -0.30V	
0.40 to -1.0V	1.00 to -1.50V	

A typical deposition scan for the range -0.15 to -0.30V vs Ag/AgCl is illustrated in Figure 5. The increase in current with each scan is characteristic of film growth formation on the electrode surface (Figure 5). The nature of the deposition profile varies with deposition range and gives some information about the quality of the deposit being formed.

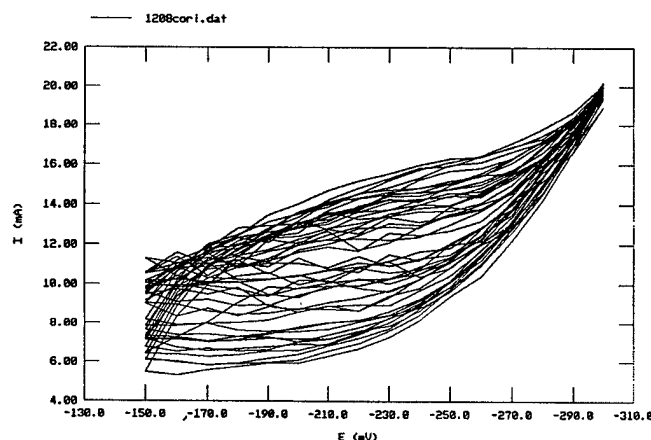


Figure 5. Pd/Ir Deposition curve for -0.15 to -0.30V on Carbon Paper

Figure 6 contains SEM micrographs of some of the deposition ranges tested. It is very evident that depositions performed at 1.60 to -0.30V and 0.60 to -0.15V show poor Pd/Ir adhesion and poor coverage of the carbon fibers that make up the carbon paper substrate. The best coverage was observed when the deposition ranges were -0.15 to -0.3V or 0.0 to -0.3V vs Ag/AgCl.

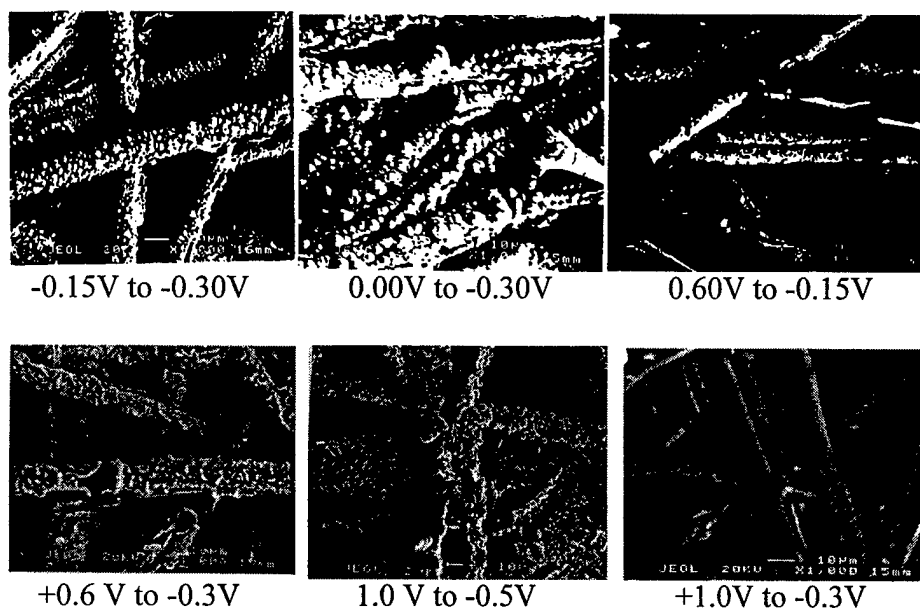


Figure 6. SEM Micrographs of Pd/Ir on Carbon Paper for several Deposition Ranges

Following every deposition, a polarization scan was performed to record the current density versus applied voltage profile. The polarization profiles for all the deposition ranges tested are depicted in Figure 7.

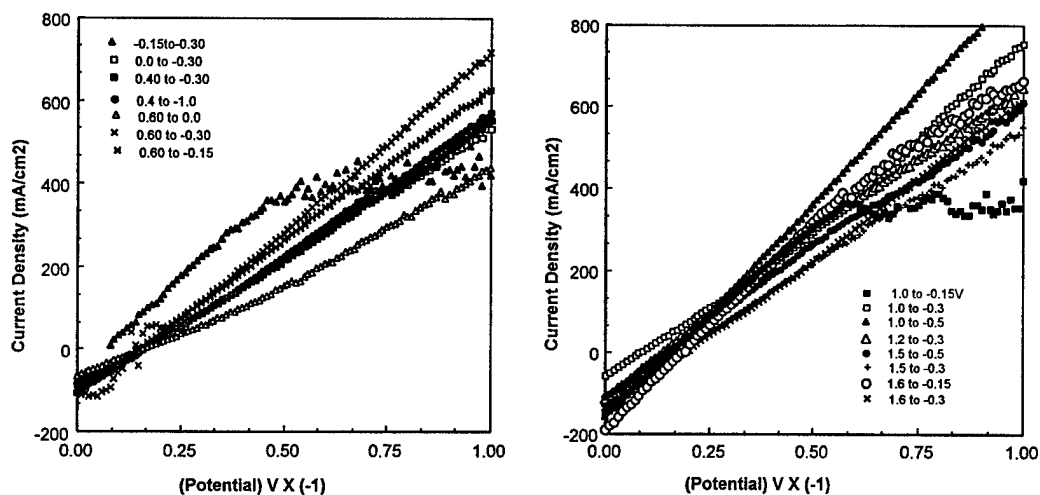


Figure 7. Polarization Curves for the Reduction of H_2O_2 for the Various Catalyst Deposition Potential Ranges

From the polarization curves (Figure 7) current density slopes were obtained for each deposition range evaluated; these current density slopes are summarized in Table II. Polarization curve slopes above $1\text{mA/mV}\cdot\text{cm}^2$ were found for six of the deposition ranges tested. These are designated by an asterisk in Table II. This data alone cannot be used to evaluate the overall quality of the electrocatalytic deposit. Surface characterization and stability must also be considered. When SEM micrographs depicting degree of substrate surface coverage, cracking and flaking and when observed stability of the catalytic deposit with repeated polarization scans are taken into account, the -0.15 to -0.30V deposition range emerges as the best.

Table II. Polarization Curve Current Density Slopes for the Reduction of H_2O_2 for the Catalyst Deposition Ranges Evaluated

Deposition Range (V)	Polarization Curve Slope ($\text{mA/mV}\cdot\text{cm}^2$)
-0.15 to -0.30	1.0050 *
0.00 to -0.30	1.0928 *
0.00 to -0.50	0.8966
0.40 to -0.30	0.7022
0.40 to -1.00	0.7366
0.60 to 0.00	0.7322
0.60 to -0.15	1.0698 *
0.60 to -0.30	1.0194 *

1.00 to -0.15	0.9558
1.00 to -0.30	1.1736 *
1.00 to -0.50	1.0900 *
1.20 to -0.30	0.9264
1.50 to -0.30	0.8504
1.50 to -0.50	0.8676
1.60 to -0.30	0.6948

Controlled Potential Deposition

Controlled potential coulometry (CPC) was investigated as a second method of catalyst deposition. The fixed applied potentials investigated were: -1.0V, -0.5V, -0.3V, 0.0V, +0.3V, +0.5V and +1.0V vs a Ag/AgCl reference electrode. Table III below summarizes the corresponding current density slopes for each controlled potential deposition tested. The highest current density slope for CPC deposition was observed at a controlled potential of -0.3V.

Table III. Current Density Slopes for the Reduction of H₂O₂ with the Controlled Potential Deposition of the Catalyst

Controlled Potential	Current Density Slope
V	mA/mV cm ²
1.00	0.0140
0.50	0.0065
0.30	0.0069
0.00	0.7030
-0.30	0.8161
-0.50	0.7811
-1.00	0.4044

Figure 8 depicts some SEM micrographs of controlled potential deposits at -0.3, 0.0 and 1.0V vs Ag/AgCl. The surface characterization analyses confirms the current density slopes in showing that a CPC deposition at -0.3V is optimum for this method, however, cyclic deposition methods are superior to CPC methods.

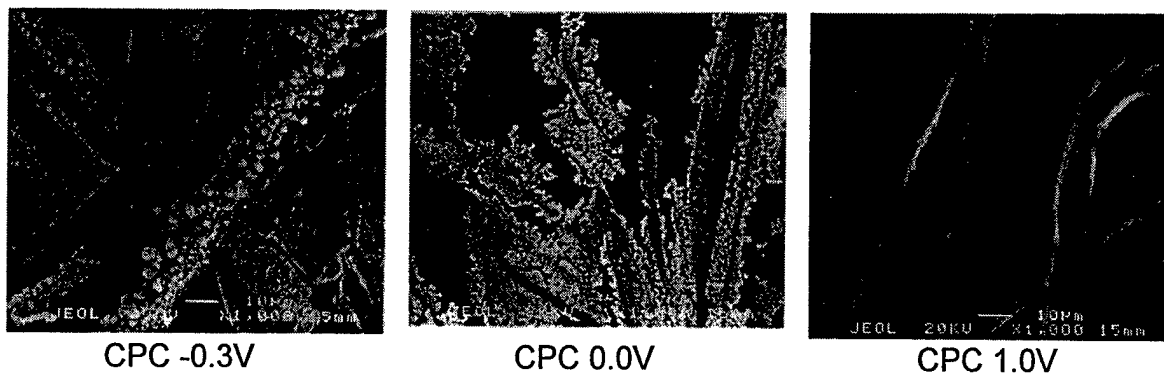


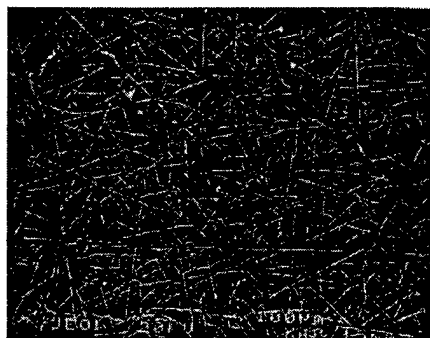
Figure 8. SEM Micrographs at Controlled Potential Coulometry Depositions

This second method of deposition, controlled potential deposition, showed deposits that were inferior to those obtained by cyclic voltammetry in the range of -0.15 to -0.30V when assessed by polarization curve slopes, degree of substrate surface coverage (SEM data), and stability (polarization curve reproducibility).

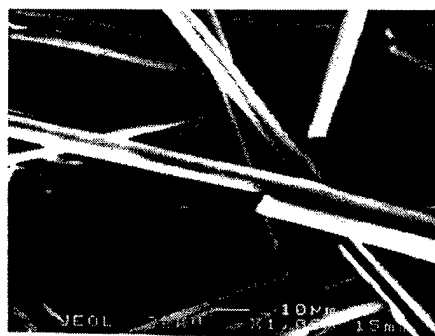
Surface Characterization

For surface characterization, Scanning Electron Microscopy / Energy Dispersive Spectrometry (SEM/EDS) analyses were performed on all depositions. Figure 9 contains SEM micrographs of the carbon paper substrate both unplated and plated with Pd/Ir (1:2 ratio) at a magnification of 40X and 1000X.

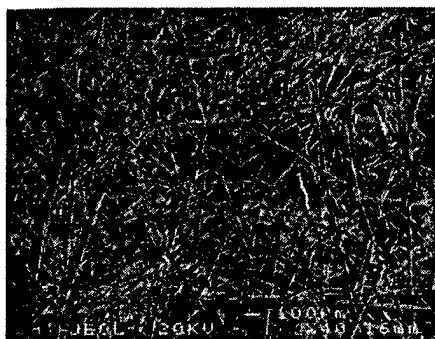
Palladium and iridium clusters are noticed at the 1000X magnification, these clusters appear well adhered to the carbon fibers. At a magnification of 40X, uneven plating is noticed. The deposition is occurring only on the top layers of the substrate and no deposition is occurring throughout the substrate. This effect is attributed to a deposition potential field that favors the outermost layers of the porous substrate. Effective electrolyte penetration of the substrate may also be a factor.



Carbon Paper - unplated 40X



Carbon Paper -unplated 1000X



Carbon Paper - Pd/Ir 40X



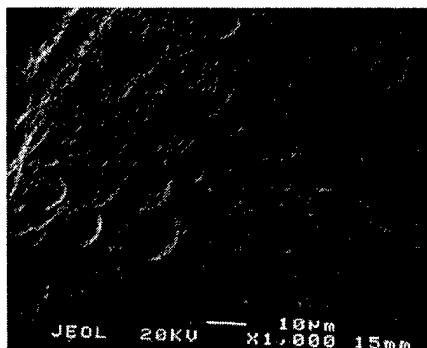
Carbon Paper - Pd/Ir 1000X

Figure 9. SEM Micrographs of Carbon Paper, unplated and plated with Pd/Ir

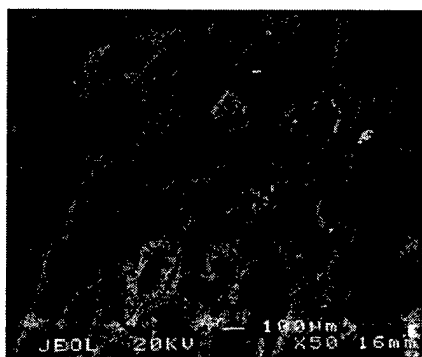
Reticulated nickel micrographs are shown in Figure 10. Both unplated Retic Ni and Pd/Ir plated electrodes are displayed. The reticulated or porous material is made up of a sponge like structure. Here again, uneven deposition of the catalyst combination throughout the substrate has been observed. The high magnification micrographs show the surface area increase once plating took place. Adhesion of the catalyst deposit is not consistent from electrode to electrode and flaking / cracking of the deposit regularly occurred.



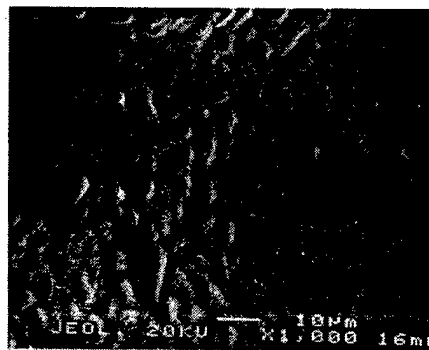
Retic Nickel - unplated 50X



Retic Nickel -unplated 1000X



Retic Nickel - Pd/Ir 50X

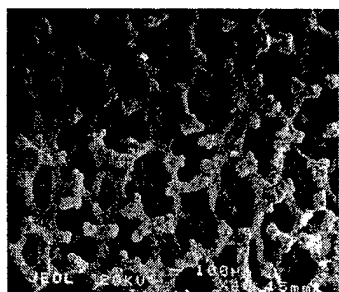


Retic Nickel -Pd/Ir 1000X

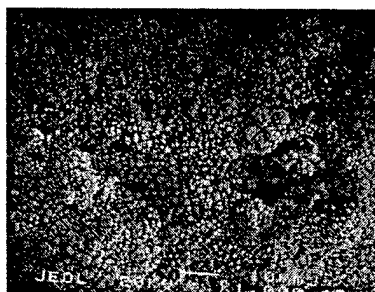
Figure 10. SEM Micrographs of Retic Ni, plated and unplated with Pd/Ir

To increase the total surface area still further and to improve the adhesion of the Pd/Ir deposit onto Retic Ni, a nanophase titanium dioxide (TiO_2) coating was applied by nebulization to the porous nickel before deposition of the Pd/Ir. SEM micrographs of the Retic Ni with TiO_2 catalyzed with Pd/Ir are shown in Figure 11. The micrographs show an increased surface area and well formed Pd/Ir clusters.

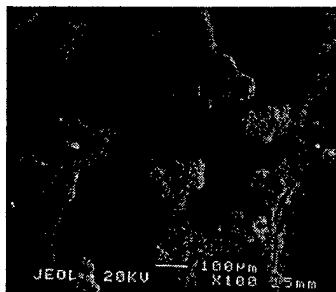
Adhesion of the catalyst deposit to the TiO_2 appears to be better than when the deposit was placed directly on the reticulated nickel. However, adhesion of the TiO_2 on the Retic Ni was no better in some cases worse than when the catalyst was deposited directly onto the Retic Ni. This poor adhesion was noted especially after a polarization curve, for the reduction of H_2O_2 in caustic electrolyte, was recorded using the electrode. The TiO_2 with the catalyst readily flaked off the Retic Ni. Unfortunately, an increase in polarization loss was also observed. This effect was attributed to the presence of the additional TiO_2 layer.



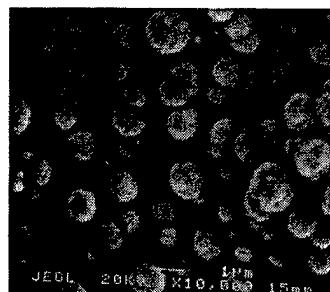
Retic Nickel, TiO_2 - Pd/Ir 50X



Retic Nickel, TiO_2 -Pd/Ir 1,000X



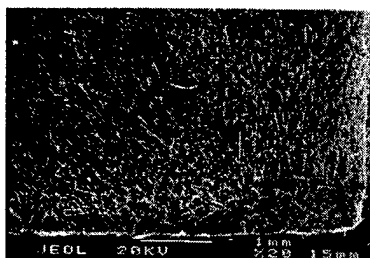
Retic Nickel, TiO_2 - Pd/Ir 100X



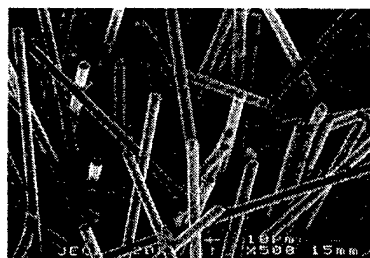
Retic Nickel, TiO_2 - Pd/Ir 10,000X

Figure 11. SEM Micrographs of Retic Nickel, TiO_2 , plated with Pd/Ir

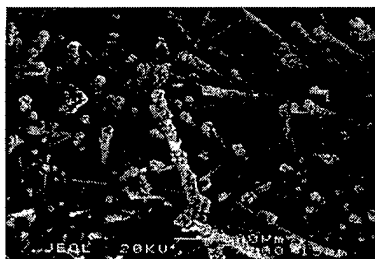
The High Electrolyte Penetration (*HEIP*) electrode is a high surface area electrode fabricated by the adhesion of carbon fibers (20×10^3 to 60×10^3 fibers/ cm^2 , $7\mu\text{m}$ diameter, 1mm length) onto a backbone (e.g. nickel) with silver conductive epoxy. This technique is a novel textile science investigated for this application in collaboration with Drs Yo Kim and A. Lewis of the Textile Sciences Department and Dr. R. R. Bessette of the Chemistry Department, UMass Dartmouth and SIR consultant to Code 8231 at NUWC. Once the electrode is manufactured (Figure 12, unplated, 20X) it looks like a carpet.



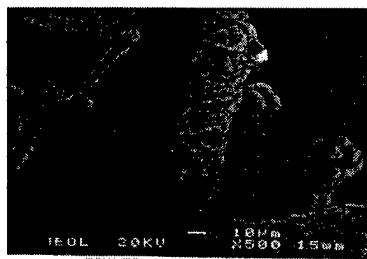
HEIP Electrode unplated 20X



HEIP Electrode unplated 500X



HEIP Electrode Pd/Ir 100X



HEIP Electrode Pd/Ir 500X

Figure 12. SEM Micrographs of HEIP Electrode, plated and unplated with Pd/Ir

At higher magnifications (Figure 12, unplatd, 500X) the aligned fibers are visible. Figure 12 also shows the SEM micrographs of the electrode with a Pd/Ir catalyst combination deposit both at a magnification of 100x and 500X. It is noticeable that not all the fibers are plated and that some of the fibers are plated only at the tips and not all the way to the base. This is a new technique that requires further investigation as the HEIP electrode has a high payoff potential for both low-rate and high-rate SFCs.

Optimum Number of Cycles for a Scan Rate of 10mV/s

The variation in polarization curve slope for the reduction of H_2O_2 on the catalyzed substrate was studied as a function of the number of cyclic voltammetry deposition cycles at 10mV/s. This variation is depicted in Figure 13. The number of cycles ranged from 5 cycles to 45 cycles. It is evident from Figure 13, that the best performance for the reduction of H_2O_2 was obtained with a catalytic surface prepared using twenty-five cycles between -0.15 to -0.30V at 10 mV/s.

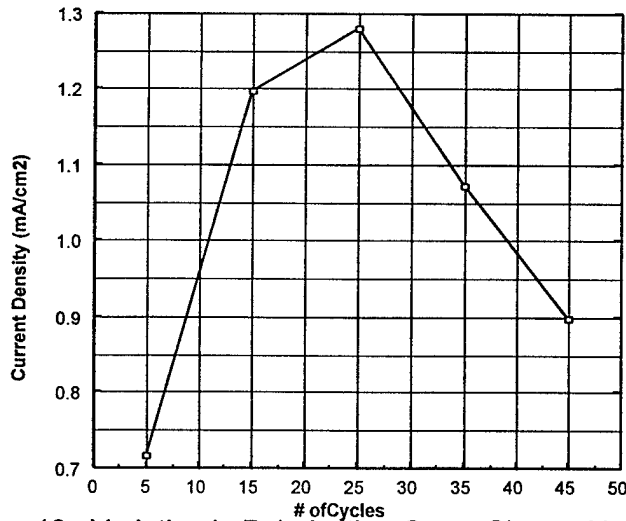


Figure 13. Variation in Polarization Curve Slope with the Number of Deposition Cycles

Scan Rate Optimization for Twenty Five Deposition Cycles

The best scan rate for twenty-five deposition cycles was also determined. The scan rate was varied from 1.00 mV/s to 65 mV/s. The polarization curve slopes for the reduction of H_2O_2 obtained are listed in Table IV.

Table IV. Variations in Polarization Curve Slope with the Scan Rate

Scan Rate (mV/s)	Polarization Curve Slope (mA/mV cm^2)
1.00	1.4428
5.00	1.1966
10.00	1.2930
15.00	1.3514
25.00	0.9524
35.00	1.3638
45.00	1.2032
55.00	1.2344
65.00	1.1480

A slow scan rate of 1.00 mV/s was found to yield the best polarization curve slope for the reduction of H_2O_2 on the catalyzed surface. Scan rates below 1.00 mV/s need to be investigated.

Application of Pd/Ir Catalyzed Cathode to a Magnesium, Seawater, Acid, Hydrogen Peroxide Full Cell Test

A Pd/Ir catalyzed cathode prepared by cyclic voltammetry deposition of the metal from -0.15V to -0.30V at 1.00 mV/s for 25 cycles was tested in a 1 1/2" X 8" cell. The cell consisted of a magnesium anode and a seawater electrolyte containing 0.1M sulfuric acid (H_2SO_4) and 0.5M H_2O_2 . Cell voltages above 1.8V were obtained at 25 mA/cm² current density over an operating time of two hours. A voltage, current, power versus time profile is given in Figure 14. Stable performance of the catalyzed cathode was obtained for replicate tests with the same cathode.

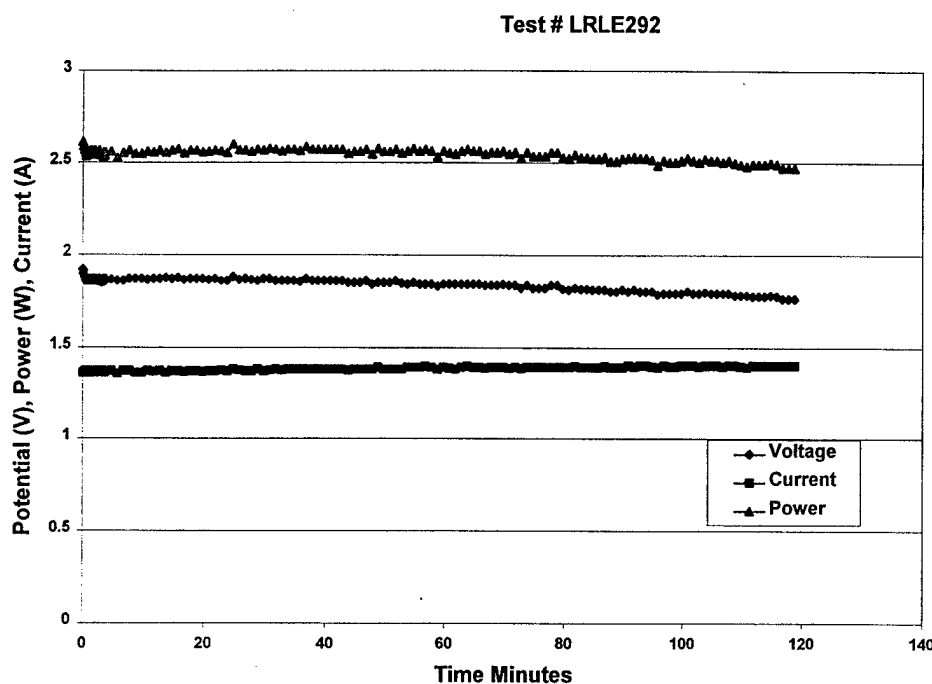


Figure 14. A Voltage, Current, Power versus Time Profile for a
Mg-SFC Full Cell Test # 292

Conclusions

A carbon paper substrate (Spectrocarb, E-Tek) was found to support the most uniform and adherent palladium and iridium catalytic deposit.

A combination of polarization curve slope for the reduction of H_2O_2 , SEM micrographs depicting degree and quality of substrate surface coverage, and observed stability with repeated polarization was used to establish the best deposition range as
-0.15V to -0.3V.

Controlled potential coulometry (CPC) deposition of the Pd/Ir combination at seven different fixed potentials was found to yield deposits at all of these potentials that were inferior to that obtained by cyclic voltammetry in the -0.15 to -0.3V range.

SEM studies revealed uneven deposition of the catalyst. The effect is attributed to a deposition potential field that favors the outermost layer of the porous carbon substrate and the ineffective electrolyte penetration of the substrate.

Uneven Pd/Ir catalyst deposition throughout a reticulated nickel substrate occurred. Adhesion of the catalyst deposit on the Retic Ni substrate was not consistent from electrode to electrode.

Application of the titanium dioxide (TiO_2) layer on the Retic Ni substrate to improve surface area and adhesion was not successful from the adhesion standpoint. Adhesion of the TiO_2 on the Retic Ni was no better than when the catalyst was deposited directly onto the Retic Ni.

Initial experiments carried out to fabricate a high electrolyte penetration (HEIP) carbon fiber electrode have been completed. Uneven catalyst plating of the fibers was obtained. Further investigation is required as the HEIP electrode has a high payoff potential for both low-rate and high-rate SFCs.

The optimum number of deposition cycles for a scan rate of 10mV/s was found to be twenty-five and a scan rate of 1.00mV/s was found to yield the best polarization curve slope for the H_2O_2 reduction. Scan rates below 1.00 mV/s need to be investigated.

Stable performance of a Pd/Ir catalyzed carbon paper cathode in a magnesium anode, seawater, acid, hydrogen peroxide cell has been demonstrated.

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